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Dissociation of ethanol molecule ions formed in charge exchange collisions with positive ions

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With 4 figures in the text

ABSTRACT

Mass spectra of C_2H_5OH have been obtained after charge exchange with slow positive ions. The intensities of the peaks have been plotted as a function of the energy absorbed by the molecule during the charge exchange. Integration of these curves gives a mass spectrum in good agreement with that obtained in electron impact. Further, the graph gives experimental information about the dissociation processes in a large molecule ion. Comparison with the corresponding graphs obtained by means of the statistical theory of mass spectra shows disagreement in several respects. The dissociation processes have therefore been interpreted without use of this theory. The low intensity of ions formed by loss of H_2O and CH_4 shows that in an electron impact experiment these ions are formed from a highly excited neutral molecule.

Introduction

The dissociation of large molecules after ionization by electron impact in a mass spectrometer has only recently been investigated theoretically. The reason is that the molecule ions dissociate in a very large number of different ways forming a large number of different fragments. Further, it has been found that the fragments may perform secondary dissociations. Owing to this the decomposition processes are quite obscure. Further, our knowledge of the mass spectra has been very incomplete. One knows very little about the excess energy which is absorbed by the molecule during the ionization process in a given electron impact. Therefore experiments are desirable that make possible an investigation of the mass spectrum of the molecule as a function of the energy that has been absorbed by the molecule.

Recently, detailed investigations of mass spectra, obtained by photon impact, have been started [1, 2, 3]. In this method, however, the experimental results [3] are complicated by the possibility of excitation. This means that at least the following five processes contribute to the observed mass spectrum of the molecule XY (Cf. [4, 5, 6]).

(1) $XY + hf \rightarrow XY^+ +$ electron without kinetic energy.
(2) $XY + hf \rightarrow XY^+ +$ electron with kinetic energy.
(3) $XY + hf \rightarrow XY^* \rightarrow XY^+ +$ electron.
(4) $XY + hf \rightarrow XY^* \rightarrow XY^+ +$ electron $\rightarrow X^+ + Y +$ electron.
(5) $XY + hf \rightarrow XY^* \rightarrow X^* + Y \rightarrow X^+ + Y +$ electron.

That process (2) is of great importance in this experiment is evident from Fig. 5 in [3]. Strong ionization of argon, caused by ionization with the ionization potentials 15.76 and 15.94 eV, was obtained in the wavelength range $hf = 15.7$ eV to $hf = 27$ eV. The energy of the ejected electron can thus have any value between 0 eV and about 11 eV. Process (3) can give a very strong ionization for certain wavelengths, which is apparent from Fig. 10 in [3] for N_2. The strong peaks at 16.2 eV and 22.5 eV seem to depend on this process. According to Weissler *et al.* this is evident from investigations of diffuse absorption bands and further it is evident from a comparison with corresponding investigations performed with ion collisions, in which the collision cross sections for ionization at these energies are low [7]. That the molecule ion formed in process (3) may dissociate according to process (4) is immediately clear. There is some evidence that process (4) is of importance in the formation of the fragment $C_2H_4^+$ with mass 28 from ethanol which will be discussed later. Process (5) has been discussed by Lagergren [6] in connection with his electron impact work. The interpretation of photon impact experiments is thus complicated by the possibility of several different processes.

The method of ionization of molecules using charge exchange during collisions with slow atomic ions seems, on the other hand, to give results [7–12] that may be interpreted with less difficulty, as the processes corresponding to (3), (4), and (5) above are inconceivable. The condition for charge exchange is that the recombination energy (RE) of the incident ion equals the ionization energy (IP) of the molecule, from which it follows that the uncertainty that is caused by process (2) does not exist. Therefore the charge exchange corresponds only to process (1). It is, of course, possible that during the charge exchange the kinetic energy of the incident ion takes part in the process, so that the condition RE = IP is not exactly satisfied. The latter complication can, however, be eliminated to a large extent by the use of slow incident ions and by the use of the following arrangement. For the analysis of the ions formed during the dissociation processes mass spectrometric analysis is used. This mass spectrometer is placed so that the beam of the incident ions and the beam of the secondary ions to be analysed in the mass spectrometer are perpendicular to each other. The discrimination in the mass spectrometer then lessens the influence of the kinetic energy and is therefore of great value in these investigations.

The theoretical discussions of the dissociation of the molecule ions in the mass spectrometer have been dominated by the statistical theory for mass spectra [13]. Using this theory, the mass spectra of several molecules have been discussed: propane [14, 15], the lower aliphatic alcohols [16], some esters [17], and some ethyl derivatives [18]. For our purposes, [14] and [16] were most complete, as they contained graphs showing the mass spectrum as a function of the absorbed energy and therefore we chose to investigate ethanol using the ion impact method.

Apparatus

The apparatus, of which a schematic diagram is shown in Fig. 1, is placed inside a large vacuum container that is evacuated with an oil-diffusion pump having a pumping speed of 5000 l/s.

The atomic ions (called A) are produced in an ion source of the Heil type [19] and are analysed in a semi-circular, inhomogeneous permanent magnet A with radius 180 mm. The kinetic energy of the ions there is between 2000 eV and 3000 eV. After the analysis, the atomic ions are retarded in a system of electrostatic lenses down to

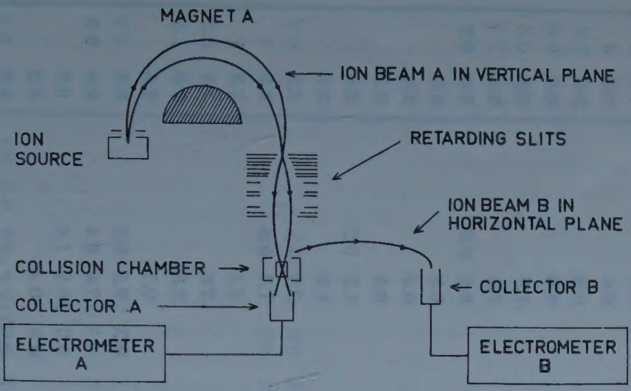


Fig. 1. Double mass spectrometer for investigation of dissociation after charge exchange. The ions A in mass spectrometer A move in a vertical plane and the ions B move in a horizontal plane. The permanent magnet core is shown only in magnet A.

the desired kinetic energy. The electrodes are given potentials such that the ion beam is focussed on the entrance slit of the collision chamber after the retardation.

The collision chamber is filled with the ethanol gas to a pressure of 1.0×10^{-4} mm Hg. The pressure is measured by means of a glass Knudsen gauge. After having passed the collision chamber the atomic ions A are collected in a collector and are measured by means of a vibrating reed electrometer A, which is at approximately the same potential as the collision chamber and therefore must be very well insulated. The ion beams A usually amount to between 10^{-8} amp and 10^{-11} amp, and therefore a resistor of 10^8 ohms is used.

In the collision chamber, ionized fragments (called B) are obtained from the gas molecules. The ions B are extracted towards one side of the collision chamber by a weak repelling voltage, are accelerated and are analysed in a permanent magnet B of the same kind as magnet A but with radius 250 mm, and are finally collected and measured with an electron multiplier followed by a vibrating reed electrometer B. The accelerating voltage is fixed at 4200 V, therefore, using the magnetic scanning techniques, the magnetic field must be varied. This variation is performed by shunting the magnet with iron, using a shaft through the wall of the vacuum container. The ion beam B is normally between 10^{-11} amp and 10^{-15} amp but is sometimes smaller.

To avoid surface charges all surfaces have been coated with collodial graphite in alcohol [20].

The retarding electrostatic lens system consists of 12 electrodes by means of which the retardation of the incident ions may be changed so that the kinetic energy of the incident ions may be varied from 900 eV down to 10 eV, although the small intensity of the incident ion beam often prevented use of lower energy than 20 eV. Details of the retarding lens system will be published.

The results of the measurements are given in Table 1. The data in the table have not been resolved into mono-isotopic spectra. The abundances are normalized to total ionization equal 100. No consideration has been given to peak 47 as it depends mainly on attachment of a hydrogen atom by secondary processes. Further, no regard has been taken of peak 18 as this peak may possibly be caused partly by background in the apparatus.

Table 1. Mass spectra of C_2H_5OH obtained in charge exchange with incident positive ions of low kinetic energy (KE).

Incident ion	Gas	KE eV	46	45	44	43	42	41	31	30	29	28	27	26	25	19	17	16	15	14	13	12	47	18
H^+	H_2	5	1.3	25.0	0.2	1.9	< 0.2		54.9	2.7	5.5	1.6	3.0	< 0.7		2.2			0.7				3.8	
H^+		15	0.9	21.5		2.1			59.0	2.7	6.0	1.7	2.7	0.2		2.4			0.9				2.1	0.3
H^+		30	0.8	23.0	0.3	1.8	0.2		58.5	2.6	5.0	1.7	2.3	0.3		2.6			0.8				2.6	0.5
He^+	He	22	0.1	0.6	0.2	5.0	11.0	1.1	4.2	1.9	23.1	1.8	14.7	9.4	0.3	0.9		0.5	17.3	7.2	0.7		0.5	0.3
He^{++}	He	15	8.5	23.4		2.4			50.2	2.3	4.1	1.5	4.3	0.4		2.7			0.5				2.4	3
He^{++}		30	8.3	24.0	0.4	2.2			49.3	2.5	4.3	1.4	4.5	0.4		1.8			0.9				1.0	4
He^{++}		300	13.2	24.6	0.3	2.0	0.1		45.7	2.3	4.0	1.2	3.8	0.5		1.6			0.6				2.2	3
B^+	BF_3	11	0.4	29.0	0.8	1.6			54.0	2.7	4.5	1.4	3.2			1.7			0.9				2.2	1.0
B^+		30	0.7	29.0	0.7	2.2			54.0	2.7	3.8	1.2	2.7			1.8			0.9				3.2	0.6
B^+		900	6.0	25.5	0.9	2.0			51.0	3.3	3.8	1.3	2.5	0.5		1.3			1.5				3.3	0.5
C^+	CO	30	6.8	50.4	0.4	2.5	< 0.2		28.2	1.0	3.3	0.6	3.5	0.6		1.3			1.3				3.8	
C^+		900	32.9	35.7	0.7	1.4	< 0.2		21.2	1.1	2.1	0.4	2.5	0.4		0.6			0.9	0.2			4.0	0.2
C^+	CO_2	30	7.4	52.1		2.6			28.4	1.0	3.3	0.6	2.8			1.1			0.8				5.3	
C^+		900	34.0	35.8		0.9			22.5	0.9	2.7	0.2	2.1			0.4			0.4				5.4	
C^+	COS	22	6.2	53.4		1.9			30.9	0.5	2.9	0.1	2.7			0.8			0.5				3.7	
N^+	N_2	15	5.7	28.6		2.1			47.7	2.1	4.6	0.9	3.9	0.5		1.9			1.7	0.2			2.6	
N^+		900	9.6	25.1		1.5			46.5	2.2	6.5	0.9	4.7	0.8		1.3			1.0				3.8	
N^+	N_2O	15	5.0	26.9		0.9			55.5	2.1	3.7	0.9	3.3			1.7			0.7				2.1	
N^+		900	8.3	21.8	0.2	2.1			47.8	2.5	6.8	1.5	3.4	1.3		2.0			1.7	0.6			4.8	
O^+	N_2O	15		10.3		4.4			51.6	2.1	10.3	2.6	12.2	0.9		3.3			2.1				1.3	1
O^+	COS	15		13.7	0.2	4.5			52.7	2.4	8.5	2.5	9.5	1.1		2.6			2.4				1.6	0.5
O^+	CO	30	0.3	12.6	< 0.3	4.6	0.6		51.5	2.8	8.5	2.6	9.3	1.3		3.3			2.3				1.8	1.5
O^+	CO_2	30		15.3		2.5			61.5	2.8	7.1	2.5	5.2	0.4		2.1			0.7				1.5	
F^+	$CBrF_3$	15		0.6	1.2	9.7	1.4		12.7	1.0	19.8	2.9	34.3	4.1		2.6		0.2	9.3	0.2			0.8	
F^+	SF_6	30		0.5	2.2	15.6	3.0		13.8	1.5	19.3	2.7	29.7	3.6		1.1			7.0	0.4			0.4	0.2
Ne^+	Ne	30		0.7	0.7	17.0	5.8		4.3	3.0	22.7	3.6	16.0	6.0		1.0		0.9	16.9	1.6			0.6	
Ne^{++}	Ne	15	20.8	48.8	0.3	0.1	0.2		23.4	0.3	1.9	0.5	0.8	0.9	0.7	0.2		0.8	0.4				4.2	
Ne^{++}		30	21.8	50.7	0.05	0.2	0.05		23.7	0.3	1.3	0.2	0.4	0.6	0.6	0.05		0.05					4.9	
Si^+	SiF_4	30	0.6	23.5	0.3	2.0			57.3	2.3	6.3	2.1	2.9			2.6			0.3				2.3	
P^+	PCl_3	11	49.3	29.7	0.4	1.5			10.4	0.3	3.8	0.4	2.7	0.03		1.2			0.2				3.7	
P^+		30	50.2	29.9	0.4	1.4	0.03		10.2	0.5	2.4	0.4	2.5	0.1		1.3			0.6				4.0	
P^+	$POCl_3$	11	50.4	29.3	0.5	1.0			10.8	0.1	4.5	0.1	2.2			1.0							3.8	
P^+		30	50.5	31.5	0.5	1.7	< 0.3		9.4	0.3	2.5	0.3	2.5			0.5							4.6	
S^+	COS	8	19.2	37.7	0.3	1.0			34.4	1.5	2.4	0.3	2.0			0.9			0.4				5.2	

Ar^+	Ar	5		0.4		10.5			40.7	1.3	11.2	3.3	26.2	1.7		4.7							0.6	0.6
Ar^+		15		0.2	0.2	10.3			38.0	1.3	10.8	3.2	28.2	1.9		5.2			0.7				0.5	0.6
Ar^+		30				10.5			38.9	1.2	11.0	3.0	27.8	1.7		4.8			1.0				0.4	0.6
Ar^+		100				10.7			36.3	1.2	11.6	3.2	28.6	2.0		4.9			1.6				0.3	0.6
Ar^+		300		0.4	0.3	11.2			32.9	1.3	12.2	3.6	28.4	2.3		4.8		0.03	2.4	0.4			0.5	0.6
Ar^+		900		0.6	0.3	10.5			33.1	1.4	12.0	4.6	27.0	2.4		4.7			2.8	0.6			0.4	0.6
Ar^{++}	Ar	30	1.5	5.0		4.1	8.5		13.6	2.2	19.4	2.1	12.1	8.7	0.4	1.1	0.6		13.3	7.3			1.4	2
Ar^{++}		300	1.9	6.0	0.2	4.2	7.7	1.3	11.6	2.0	18.2	1.7	10.6	8.2	0.8	0.8	0.5	0.4	13.5	8.4	0.9	0.4	0.6	0.3
Br^+	CBr_2F_2	30	1.0	25.5		0.3			67.1	2.0	2.0	0.3	1.3			0.6							5.4	
Kr^+	Kr	15		9.0		1.3			64.3	2.3	11.6	3.5	3.2			4.7							1.6	
Kr^{++}	Kr	15	0.6	1.7	0.9	12.1	5.5	0.4	7.7	4.3	23.0	3.6	19.0	4.2	0.07	1.5	0.9	0.8	11.6	2.1			0.8	0.6
Kr^{++}		30	0.7	1.7	1.3	13.6	5.8		7.9	4.0	20.4	3.2	15.4	4.5	0.1	1.3	0.7	0.8	15.7	2.8			0.8	0.3
J^+	J_2	8	36.2	23.6					34.3		3.9		0.9			1.0							4.2	
J^+		30	50.5	22.0	0.7	0.2			22.8	0.5	1.4	0.2	0.7			0.7			0.1				4.4	
J^+		900	47.2	30.3	0.6	0.4			18.4	0.6	1.0	0.3	0.7	0.1		0.4			0.4				3.3	
Xe^+	Xe	15	0.4	21.6					74.4	1.9	1.0	0.4				0.4							3.0	
Xe^{++}	Xe	15	0.7	10.4	0.4	5.1	1.3		32.9	2.3	13.8	1.8	16.1	2.1		2.3	0.2	0.2	9.3	0.9			1.8	1
Xe^{++}		30	0.6	8.2	0.4	6.4	1.6		27.4	2.3	17.0	1.9	19.9	2.2		1.8	0.2	0.2	9.2	0.8			1.3	0.4
Hg^+	Hg	10	36.9	7.1		2.3			34.1	1.5	6.0	1.0	6.6			3.2			1.3				3.8	
Hg^+		23	47.6	7.8		1.7			23.1	1.3	7.2	1.1	7.5			2.0			0.9				3.6	
Hg^+		100	54.8	10.6	0.7	1.4			20.9	0.9	3.9	0.9	3.2	0.3		1.5			0.8				3.7	
Hg^+		300	53.2	15.0	0.5	1.4			19.4	0.8	3.2	0.8	3.2	0.3		1.4			0.7				3.9	
Hg^+		900	49.2	18.8	0.7	1.6			18.8	0.8	3.4	1.1	3.2	0.3		1.4			0.7				3.5	
Hg^{++}	Hg	100	13.6	19.8	0.6	5.3	1.0		26.1	1.6	8.4	2.3	12.9	1.9		2.5			3.0	0.8			1.8	0.4
H_2^+	H_2	11	6.3	21.1	0.3	3.5			46.4	1.6	7.7	1.9	6.7	0.3		3.3			0.9				6.0	1.5
CH^+	CH_4	30	41.2	36.0	0.8	1.3			14.7	0.4	2.0	0.3	1.6	0.04		1.0			0.4				4.5	
CH_2^+	CH_4	15	37.2	37.1	0.6	1.5			10.8	0.4	4.5	0.6	3.9			2.9			0.6				4.8	
CH_3^+	CH_4	15	6.0	55.1		3.0			12.3	0.6	7.6	1.0	7.6			5.6			1.3				3.0	
CH_4^+	CH_4	15	26.6	34.5	0.3	0.1			26.7	0.6	7.4	0.2	0.6			2.6			0.3				4.6	
CO^+	CO	11	< 0.4	12.5	< 0.4	1.3			64.3	3.2	8.0	2.6	1.6			5.1			< 0.4				1.6	< 0.4
CO^+	CO_2	15	1.2	12.3	0.5	2.5			56.2	2.5	9.8	2.8	4.8	0.6		6.2			0.6				3.1	
CO^+	COS	15	0.3	13.5		1.3			64.2	2.6	9.0	2.9	2.2			4.2							2.2	
N_2^+	N_2	15	2.0	2.4	0.2	7.5	< 0.2		40.8	1.4	10.4	3.1	23.2	1.6		6.1			1.1				1.4	2
N_2^+		900	1.8	5.8		10.1			36.2	2.0	11.9	2.7	19.0	2.5		4.2			3.1	0.7			1.8	
NO^+	N_2O	30	18.5	24.7	0.6	2.7			34.1	1.7	6.1	1.5	6.3	0.6		1.9			1.4				4.6	1
HS^+	H_2S	30	39.9	24.4					28.1		3.8		2.4			1.4							7.8	
H_2S^+	H_2S	30	58.8	20.0		0.2			15.3		2.9		1.1			1.6							9.4	
CO_2^+	CO_2	30	0.7	16.2		1.0			67.6	2.4	6.4	2.4	1.4			2.0							2.7	0.5
N_2O^+	N_2O	22	0.6	19.5		0.3			70.9	2.5	3.2	1.1	0.9			1.1							3.9	

As mentioned above, the kinetic energy of the incident atomic ion has small influence on the energy transformed during the charge exchange from the ion to the molecule, provided that the velocity of the atomic ion is small enough. As shown in the table, the measurements usually have been performed at the kinetic energy 10 eV. That this kinetic energy is small enough is clear from, for instance, the measurements with Ar^+. When the kinetic energy is varied from 5 eV to 30 eV, the mass spectrum is only slightly changed. The fluctuations in the table seem to depend on accidental errors, as the ion current A is very weak at this strong retardation. For high kinetic energies some systematic deviations can be observed. The velocity dependence just described is characteristic for most of the ions that have been used in this investigation. On the other hand, it is evident from the table that for C^+ the mass spectrum changes considerably when the kinetic energy is changed from 30 eV to 900 eV. The reason is probably that RE 10.00 eV, which is lower than IP for the ethanol and therefore normally without interest, may cause charge exchange at the high kinetic energy, so that the molecular ion with mass 46 is formed in larger quantities. A similar explanation may be given to the corresponding phenomenon with B^+, N^+, and S^+. These measurements seem to prove that the velocity of the incident ions usually is sufficiently low, so that their kinetic energy does not take part appreciably in the energy balance during the charge exchange.

As the pressure in the collision chamber amounts to 1.0×10^{-4} mm, secondary processes are possible. This is especially evident from fragment 47 that is obtained solely in this manner. Inspection of Table 1 shows that peak 47 seems to depend on the sum of the intensities of peaks 46 and 45 and is therefore fluctuating, although the pressure in the collision chamber is held approximately constant during all measurements. The pressure dependence of the mass spectra has been investigated separately using the noble-gas atomic ions. The result of this investigation is that when the pressure was diminished to 3×10^{-5} mm, peak 47 decreased but no change could be observed for the other peaks. When the pressure was increased to 5×10^{-4} mm or more peak 47 increased very rapidly by a factor of more than ten. Peak 19 increased by a factor of three, but the remaining peaks did not change so much. We therefore feel sure that the main peaks cannot depend to any considerable extent on secondary processes in the collision chamber.

Mass spectrum as a function of absorbed energy

The main results of this paper are given in Fig. 2, which shows the mass spectrum as a function of the energy absorbed by the molecule. The curves are normalized so that the sum of their ordinates at each energy is equal to 100.

When constructing these curves we have assumed that the energy absorbed by the molecule equals the RE of the atomic ion. Further, we have assumed that the mass spectrum obtained in collision with a certain ion depends exclusively on the RE of the ion and not on the nature of the ion. This assumption is of course not generally valid, but using our apparatus it may be regarded as valid with good approximation. The condition is, of course, not satisfied if the charge exchange takes place in a collision such that the distance between the molecule and the ion is small, but after such a collision the secondary ions will have some initial velocity in the direction of the incident ions and therefore they will never reach collector B in mass spectrometer B owing to its discrimination. The processes that we are able to observe in our apparatus are therefore characterized by large distances between the colliding particles.

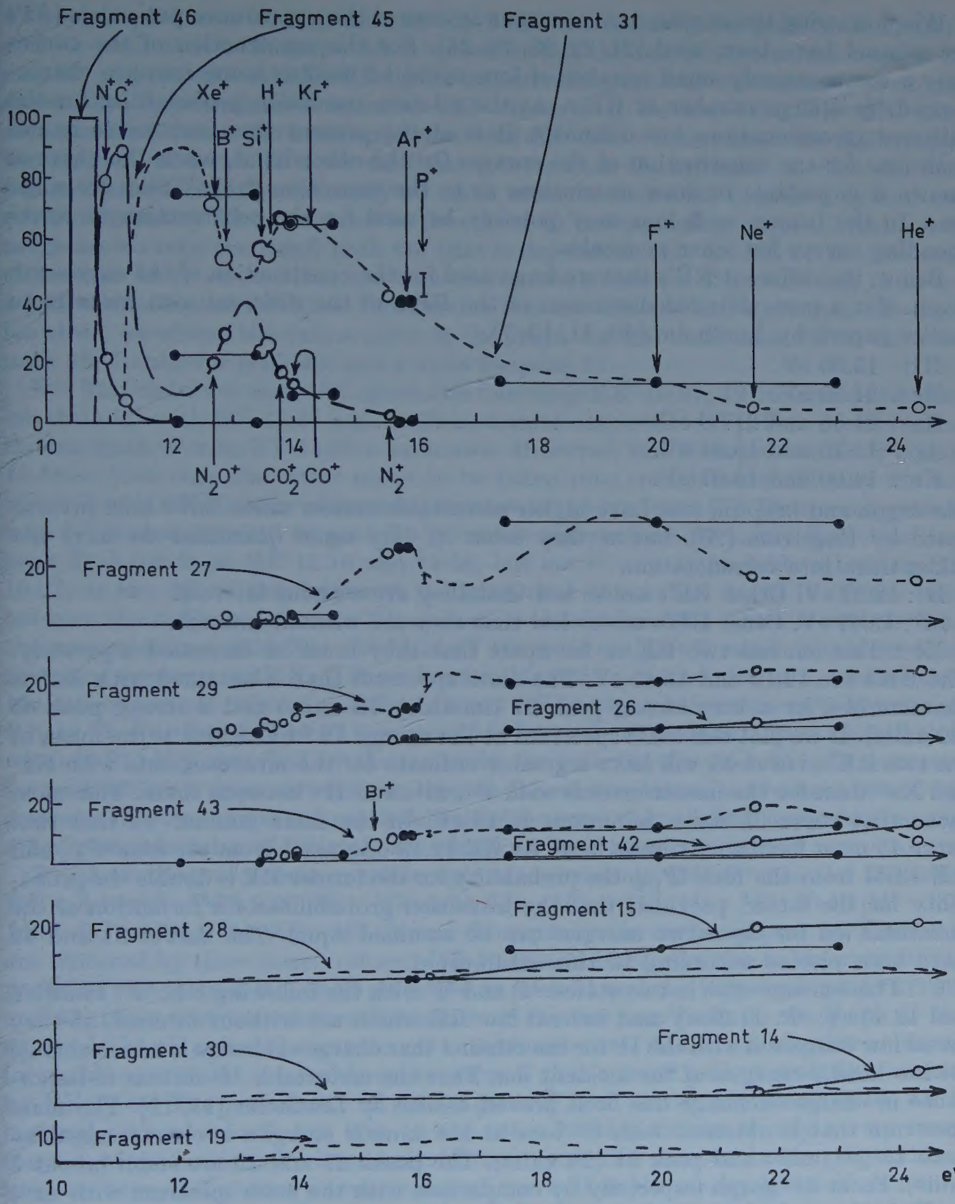


Fig. 2. Mass spectrum of C_2H_5OH as a function of energy (eV).

In such cases the nature of the incident ions is of course without any importance and the charge exchange is determined only by the RE of the ion. The validity of our assumption can be examined by a discussion of the curves in Fig. 2. If the assumption is erroneous, it would generally be impossible to draw a continous curve through the experimental points.

When drawing the curves, earlier measurements of the appearance potentials (AP) for ethanol have been used [21, 22, 23, 24, 25]. For the construction of the curves only a comparatively small number of ions could be used as some ions are characterized by a large number of RE's. As the relative transition probabilities for the different recombinations are unknown, it is at the present time impossible to use such ions for the construction of the curves. On the other hand, when the curve is known it is possible to draw conclusions as to the transition probabilities for some ions. In the future, such ions may possibly be used for the construction of corresponding curves for other molecules.

Below, the different RE's that we have used for the construction of the curves are given. For a more detailed discussion of the RE's of the different ions we refer to earlier papers by Lindholm [10, 11, 12, 7].

H^+: 13.60 eV.
He^+: 24.58 eV.
Ne^+: 21.56 and 21.66 eV.
Ar^+: 15.76 and 15.94 eV.
Kr^+: 14.00 and 14.67 eV.

The argon and krypton ions have higher metastable states, which have been investigated by Hagstrum [26], but as they occur in very small quantities we have not taken them into consideration.

B^+: 12.92 eV. Other RE's are so low that they are without interest.

Si^+: 13.47 eV. Other RE's are so low that they are without interest.

Xe^+: This ion has two RE so far apart that they must be discussed separately. The RE's are 12.13 and 13.44 eV. The mass spectrum that is obtained with Xe^+ is characterized by a very strong peak 31 (intensity 75 units) and a strong peak 45 (22 units). If we plot this mass spectrum at the energy 12.8 eV, which is the mean of the two RE's, curve 31 will have a greater ordinate for the measurements with Kr^+ and Xe^+ than for the measurements with B^+, Si^+, and H^+ between them. This must mean that curve 31 has a minimum at 13 eV. In the same manner we find that curve 45 must have a maximum here. As RE 12.13 originates from the ions $^2P_{3/2}$ and RE 13.44 from the ions $^2P_{1/2}$, the probability for the former RE is double the probability for the latter, provided that the transition probabilities for formation of the molecular ion for these two energies can be assumed equal. The curves 31 and 45 have been plotted according to this assumption.

C^+: This ion can exist in two states: ^4P and ^2P with the following RE: ^4P: 16.58 eV and 12.40 eV; ^2P: 11.26 eV and several low RE which are without interest, as they are so low compared with the IP for the ethanol that charge exchange is inconceivable for low kinetic energies of the incident ion. That the metastable ^4P state is of importance in charge exchange has been proved earlier by Lindholm [11, 12]. The mass spectrum that is obtained with C^+ ions at low kinetic energies is characterized by peak 45 (50 units) and peak 31 (28 units). The peaks 27 and 29 are small (about 3 units). From the graph (especially by comparison with the mass spectrum with Ar^+) we find that peaks 27 and 29 can be explained with RE 16.58. This RE also explains a small part of peak 31, which can be assumed to be approximately as great as peak 27 and peak 29. Taking this into consideration we reduce peak 31 to about 25 units. Let us now discuss how the main parts of peaks 31 and 45 are formed. The RE that are of interest are 11.26 and 12.40, but as the excited state ^4P exists only in small quantities (also RE 16.58 is of only secondary importance), the main part of the peaks depends on RE 11.26. To begin with, if we assume that RE 12.40 is completely without importance, we find that for RE 11.26 the intensity for peak 31 is 25 units and for peak 45 it is 50 units. After normalization the relative intensities become 33 and 67, respectively. At this RE the formation of fragment 45 consequently predominates. The predominance becomes still stronger if we also take RE 12.40 into consideration. From the mass spectrum with Xe^+ it is evident that, for this energy, the ordinate of curve 31 is several times greater than the ordinate of curve 45. This means that the relative intensity 67 units must be increased considerably and the relative intensity 33 units must be decreased in corresponding degree. Finally it is necessary to take the small peak 46, that is dependent only on RE 11.26, into consideration. If we assume that the transition probabilities for RE 16.58 and 12.40 are equal, which is plausible since those transitions are allowed and start from the same ion state, we obtain the values given in the graph for RE 11.26, namely: 89 units for peak 45, 7 units for peak 46, and 4 units for peak 31.

N^+: The main ion state, ^3P, gives the following RE: 10.97, 12.16, and 14.54. The ion state ^1D with RE 12.87 and 14.06 is of small importance [7]. The importance of the ion state ^1S with RE 15.03 is unknown. However, this RE approximately equals 14.54 so that only the latter needs to be taken into consideration. Finally the ion state ^5S with RE 20.34 is without importance in the ion beam [7]. The mass spectrum with N^+ is characterized by peak 31 (55 units) and peak 45 (27 units). It is clear that peak 31 depends on RE 12.16 and 14.54, but not to any appreciable extent on RE 10.97, as the AP of this fragment is higher than this value. At 12.16 eV the ratio between the ordinates of curve 31 and curve 45 is at least 3.4 which is evident from the mass spectrum with Xe^+. At 14.54 eV the ratio is about 7, which is evident from the mass spectrum with Kr^+. If we use for this ratio a mean value of 5, we find that 11 units of peak 45 depend on RE 12.16 and RE 14.54, and therefore only 16 units on RE 10.97. Further, RE 10.97 is responsible for peak 46 (5 units). Thus we find that when 10.97 eV is absorbed by the molecule, the intensity for peak 45 is 16 units and for peak 46 it is 5 units. After normalization the relative intensities become 76 and 24, respectively. The numerical results obtained here are only slightly dependent on any other plausible value of the ratio for which we have taken the value 5.

P^+: According to recent spectroscopic measurements [27] P^+ has the following RE's: 8.14 ($^3P-{}^2P$); 9.05 ($^3P-{}^2D$); 9.24 ($^1D-{}^2P$); 10.15 ($^1D-{}^2D$); 10.48 ($^3P-{}^4S$); 10.81 ($^1S-{}^2P$); 16.14 ($^5S-{}^4S$). (Some discrepancies in earlier papers by Lindholm are removed by these lower values.) RE 10.48 and 10.81 give rise to the very strong peaks 46 and 45, and RE 16.14 gives rise to peak 31 and the very weak peaks 27, 29, and 43. If we plot the relative intensities of the last four peaks in the graph at the energy 16.14 eV curve 31 seems to get a maximum here. As there is no other evidence for such a maximum, a possible explanation is that a small part of peak 31 is caused by RE 10.81. The probability of such a process is of course very small as its AP is higher by about 0.5 eV, but it is on the other hand sufficient if only a very small fraction of the incident P^+ ions in the ^1S state cause this process. In the graph, therefore, we have also plotted a lower value of curve 31 at the energy 16.14 eV and have drawn curve 31 through this point. This point corresponds to the higher values of the curves 27, 29, and 43. It is seen that in spite of the uncertainty some information can be obtained as to the ordinates of the curves 29 and 27 at the energy 16.14 eV.

F^+: This ion has three RE's: 17.42, 20.01, and 22.98. Earlier the F^+ ions were obtained from BF_3, but owing to the small intensity we have now used SF_6 and $CBrF_3$. The ions from these two gases seem to have mainly the same properties. As nothing is known regarding the abundance of the different RE, we plot the mass spectrum for the mean value of the RE, 20 eV.

Br^+: The following ion states predominate: ^3P, with RE about 12 and ^1D, with RE about 13 eV. If we assume that the contributions from these RE are equal, we can compute from our graph that fragment 31 has an intensity about 2.8 times the intensity of fragment 45. These predictions agree well with the observed mass spectrum in Table 1. The third ion state ^1S with RE 14.87 and 15.32 occurs in only small quantities [12]. It is responsible for peak 27 (1.3 units) and peak 43 (0.3 units). Assuming that curve 27 is rising linearly in the vicinity of this energy we can use the ordinate of curve 27 at 15.32 eV to compute the ordinate of curve 43 at this energy to be 5 units. The AP for this fragment is thus, according to our curve, lower than 15.32 eV but higher than 14.67 eV (Kr^+).

N_2^+: According to [7] the main part of the N_2^+ ions are in the ground $X\,^2\Sigma_g^+$ state with RE 15.58 and only a small part in the $A\,^2\Pi_u$ state with RE 16.69. We have therefore plotted the mass spectrum from bombardment with N_2^+ at the energy 15.58 eV in the graph and observe good agreement with the corresponding mass spectrum with Ar^+.

CO^+: According to [7] the main part of the CO^+ ions are in the $X\,^2\Sigma^+$ state with RE about 14.0. If the mass spectrum with CO^+ is plotted in the graph at the energy 14.0 eV, good agreement is obtained with the mass spectrum with Kr^+.

We have now finished the discussion of the measurements with the ions that can be used directly for the construction of the curves in the graph. For this construction we have also used the AP measurements that were made earlier.

Curve 46: The left-hand part of curve 46 must start from the mass spectrometric AP. Cox [25] obtained the value 10.4 eV. This value is lower than the other measurements: 10.6 eV [24], 10.7 eV [16], 11.3 eV [22], 11.8 eV [23]. The low value is supported by measurements made by photon impact by Watanabe [28], who has obtained 10.45–10.55 eV. Further, Cox's value for *n*-propanol agrees well with measurements with photon impact [1, 2]. Our results with S^+ and Hg^+ indicate a value higher than 10.43 eV. We have therefore chosen 10.5 eV.

Curve 45: The left-hand part of the curve must start from the mass spectrometric AP. Here we have chosen the value given by Cox: 10.8 eV. Also in this case, this value is lower than the others: 11.0 eV [22, 16]. Even though we have used the lowest AP value that has been measured, it is evident that curve 45 rises very steeply here. It is impossible to observe any indication of the slow rise that is predicted by the statistical theory for mass spectra.

As mentioned above, we have obtained a second maximum at about 13 eV. The existence of this maximum is strongly supported by Cox's observation of a higher AP value for this fragment at 12.7 eV.

Curve 43: The following AP values have been measured: Cox, 11.6, 12.9, 13.4, and 15.7; Kambara *et al.*, 13.3; Friedmann *et al.*, 14.5. From our curve should follow an AP at about 15 eV, where our curve is rising steeply. The curve has, however, a long tail, which may perhaps be described with an AP at about 13 eV. We have no idea whether this tail is real or whether it perhaps is due to small quantities of hydrocarbons in the apparatus.

Curve 31: The left-hand part of the curve must start from the mass spectrometric AP. Also in this case we have chosen the lowest AP value that has been observed, 11.3 eV [22]. Other measurements: 11.5 eV [25], 11.6 eV [16], 11.9 [23].

As mentioned above our measurements suggest a second maximum at about 14 eV. This maximum is strongly supported by the AP that Cox [25] has observed at 13.9 eV.

Curve 29: The observed AP values 12.3 eV [16], 13.2 eV [25, 23] agree rather well with the rising part of our curve.

Curve 27: The observed AP values: 14.0 eV [23], 14.5 eV [25, 22], 14.7 eV [16] agree rather well with the rising part of our curve. Further Cox has observed an AP at 17.5 eV which possibly has a connection with the great intensity that we have obtained with F^+.

Curve 19: Our curve begins to rise at a somewhat lower energy than the observed AP 14.5 eV [22].

Curve 15: The observed values are: 15.0 eV [25], 15.4 eV [23], and 15.5 eV [22]. However, our curve begins to rise only between 16.14 eV and one of the RE of F^+.

Curve 14: Our curve begins to rise between 21.66 eV and 24.58 eV. The observed AP are lower: 16.5 eV [22] and 16.1 and 18.7 eV [25].

After this discussion of the construction of the curves we shall consider the mass spectra with the other ions, which cannot be used for the construction but which may easily be explained by means of our curves and thus support our results.

S^+: The mass spectrum with S^+ is of value for checking our curves. S^+ ions in ^4S state give RE 10.36 and in ^2D state RE 11.05 and 12.20. Comparing with the graph, we find that the mass spectrum ought to consist of peaks 46, 45, and 31. If the transition probabilities can be assumed to be equal for RE 11.05 and 12.20, the intensities of peaks 45 and 31 ought to be equal. From Table 1 it is evident that the mass spectrum agrees with these predictions. For higher velocities of the incident ions, peak 46 increases. This indicates that AP of fragment 46 is higher than 10.36 eV.

Cl^+: This ion has three states: ^3P, ^1D, and ^1S, giving three RE's: about 13.0, about 14.4, and about 16.4. RE 16.4 is practically without interest [11], and the number of ions with RE 14.4 is less than the number with 13.0, but not negligible [7]. If we assume that 20 or 30 % of the ions have RE 14.4 and the rest RE 13.0, we find easily from the curves in the graph that peak 31 should be about $2\frac{1}{2}$ times as intense as peak 45, and that the other peaks are relatively small. This agrees well with the result in Table 1.

Hg^+: This ion has not been used earlier. Its RE's are 10.43 ($6s\,^2S - 6s^2\,^1S$) and 14.83 ($6s^2\,^2D_{5/2} - 6s^2\,^1S$) [29]. RE 10.43 causes peak 46 and RE 14.83 causes all other peaks. Higher RE's are probably of minor importance as the mass spectrum computed in this way agrees well with the observed mass spectrum in Table 1. The increase of peak 46 with increasing velocity indicates that AP of peak 46 is slightly higher than 10.43 eV.

H_2^+: According to [7] (see also [30]), H_2^+ has RE between 16.4 and 17.4 eV and between 13 and 14 eV. RE 16.4–17.4 gives, according to the graph, the fragments 31, 29, and 27 with about the same intensity. As peaks 29 and 27 have the intensity 7 units, it follows that 7 units of peak 31 are due to this RE. As the measured intensity of fragment 31 is 46 units, only 39 units depend on RE 13–14. This RE also causes peak 45 (21 units). The ratio 39 units/21 units = 1.9. If we compute from the graph the area below curves 31 and 45 between 13 eV and 14 eV we obtain the ratio 2.0. The agreement between the theoretically computed and the experimentally observed ratio must be considered as satisfactory. According to the table, fragment 46 is also obtained. The explanation must be some lower RE, possibly transition to the repulsive $^3\Sigma_u^+$ state.

CO_2^+ and N_2O^+: These ions have not been used earlier. With the assumption that their RE's agree with their IP (13.80 and 12.71 eV, respectively), good agreement with the mass spectra with Kr^+ and CO^+ and with the mass spectrum with Xe^+, respectively, is obtained. *Added in proof:* I. E. Dayton, F. W. Dalby and R. G. Bennett (J. Chem. Phys. *33*, 179 (1960)) have found that the upper electronic state of N_2O^+ has a very short lifetime, which supports our assumption.

CH_4^+: The RE's for this ion are unknown. From the mass spectrum in the table it is evident that the RE range must lie between 10.4 eV, or lower, and about 12 eV. Thus the strong peaks 46, 45, and 31 are explained. This is in agreement with an earlier observation [10] that when CH_4 (IP 13.2) is bombarded with CH_4^+ the cross sections for charge exchange are surprisingly small.

H_2S^+: IP for this ion is 10.5 eV. The mass spectrum has a very strong peak 46, which shows that the RE of the ion also amounts to about 10.5 eV. Besides there are peaks 45 and 31, which shows that probably the RE range extends to a somewhat higher value than 10.5 eV. As the other peaks are small the higher RE in H_2S^+ are probably of minor importance.

O^+: This ion is the most complicated atomic ion that has been used in our investigations, as it has several RE from 13.62 up to 18.64, all of which seem to be of importance. It is therefore, of course, possible to explain our observed mass spectrum but no information of value can be obtained in this manner.

J^+: This ion has not been used earlier. Its RE's are: 14.58 and 13.56 ($^1S-{}^2P$); 12.24 and 11.22 ($^1D-{}^2P$); 11.42, 11.34, 10.54, 10.40, 10.32, and 9.52 ($^3P-{}^2P$); and possibly also 13.73, 12.96, and 12.84 ($^5S-6s\,{}^4P$). Martin and Corliss [63] have found lines corresponding to transitions from ^1D and ^1S to the ground state of the ion, but our mass spectrum shows that the lifetime of these states must be longer than the transit time in mass spectrometer A.

Doubly charged atomic ions.—The processes $A^{++}+B\rightarrow A^{+}+B^{+}$ are characterised by the electrostatic repulsion between the singly charged ions obtained in the partial charge exchange. If the charge exchange takes place when the distance between the colliding particles is small the effective RE will be considerably lower than the spectroscopically determined RE [32, 33, 34]. According to these theoretical computations the collision cross section may be rather large. As the electrostatic repulsion will cause a considerable initial velocity the cross section that we are able to observe in our apparatus will, however, be rather small owing to the discrimination in the mass spectrometer. If on the other hand the charge exchange takes place when the distance between the colliding particles is large, the effective RE will approximately agree with the spectroscopically determined RE. No theoretical computations of the collision cross section have been performed in this case, but provided the energy resonance is exact the cross section is probably comparatively large (cf. measurements of cross sections of 2002 reactions [35]).

He^{++}: This ion has the following RE: 54.4 eV, 13.6 eV, 6.05 eV and lower. As fragments with low mass numbers (for instance 14, 13, and 12) are absent in this mass spectrum, the highest RE is evidently of small importance. If the charge exchange takes place when the distance between the colliding particles is large the mass spectrum with He^{++} can be assumed to be identical with the mass spectrum with H^+. If on the other hand this distance is small, the effective RE will be lower, causing increased intensity of peak 46. These predictions agree very well with the mass spectrum in Table 1. According to this interpretation the effective RE of He^{++} in collisions with polyatomic molecules seems to amount to about 13.6 eV.

This seems to be of interest for the interpretation of the mass spectrum of acetylene produced by 5.1 MeV alpha particles [36], and further for the interpretation of certain primary processes in radiation chemistry.

Ne^{++}: This ion can exist in three states: ^3P and the metastable states ^1D and ^1S. The relative abundances of these states are unknown. All states give approximately the same RE. Recombination of a $2p$ electron gives the following RE: 41.1, 44.2, and 48.0 eV, respectively. Recombination of a $3s$ electron gives: 13.2–13.9 eV, and recombination of a $3p$ electron: 10.6 eV and lower. As fragments with low numbers are absent in the mass spectrum, recombination of a $2p$ electron seems to be without importance. The mass spectrum may easily be interpreted with the assumption that the probability of recombination of a $3p$ electron is much higher than recombination of a $3s$ electron. That the low RE in Ne^{++} are important for the interpretation of charge exchange phenomena can further be seen from measurements by Flaks and Solov'ev [37]. In their investigation of partial charge exchange of Ne^{++} in Xe, Kr, Ar, and He they found the largest cross section in Xe (IP = 13.4 eV).

Ar^{++}: Recombination of a $3p$ electron gives RE 27.6, 29.4, and 31.7 eV, respectively. For recombination of a $3d$ or $4s$ electron RE is 11.4 eV or lower, down to 6.6 eV. The transition probability for transitions with low RE seems to be rather small and therefore the high RE are of greatest importance. The mass spectrum with Ar^{++} agrees rather well with the mass spectrum with He^+ which shows that the effective RE amounts to about 24 eV for the high RE. When making this comparison we have neglected the peaks 46, 45, and 31, which depend on RE 11.4 eV.

Kr^{++}: Recombination of a $4p$ electron gives RE 23.9–28.7 eV. For recombination of a $5s$ electron, RE is 11.2–10.2 eV and for recombination of a $4d$ electron, 10.3 eV or lower. The transition probability of the transitions with low RE seems to be rather small which is proved by the small peaks 46, 45, and 31. The mass spectrum with Kr^{++} agrees well with the mass spectrum with Ne^+ which shows that in this case the effective RE is about 21 eV or possibly a little lower.

Xe^{++}: Recombination of a $5p$ electron gives RE 19.9–25.8 eV. For recombination of a $6s$ or $5d$ electron, RE is 11.1 eV or lower. The transition probability for transitions with low RE seems to be very small, which is proved by the very small peak 46. We must therefore try to explain the mass spectrum by means of an effective RE somewhat lower than 19.9 eV. This proves to be impossible. However, if we assume that peaks 31 and 45 are caused by Xe^+ ions the mass spectrum may be explained without difficulty. The Xe^+ ions are probably formed by charge exchange before the ions enter the collision chamber. This explanation has been verified by a separate investigation of the pressure dependence of the mass spectrum. Of course this process is conceivable also for Kr^{++} but as RE in this case is considerably higher ($\approx$ 21 eV) the probability for formation of Kr^+ is so small that the process is of only minor importance.

Mass spectrum using electron impact

The mass spectrum that is obtained using electron impact may be computed by integrating our curves in Fig. 2. This method has been used earlier [13, 14, 15, 16] in order to compare the statistical theory with the experiments. An electron with kinetic energy of the order of magnitude that normally is used in mass spectrometers, i.e. about 100 eV, can give different quantities of energy to a molecule, the mean of which is usually estimated to be of the order of 10 eV. This energy distribution has

Table 2. Comparison of calculated and observed electronic mass spectra.

m/e	Species	Obs., Friedman	Calc., this paper	Calc., Friedman
46	$C_2H_5OH^+$	7.4 P	6.3	13
45	$C_2H_4OH^+$	16.3	18.2	9
43	$C_2H_3O^+$	3.2	3.3	
31	CH_2OH^+	43.0	50.6	47
30	CH_2O^+	2.2	1.0	
29	$C_2H_5^+ + COH^+$	7.9	7.7	26
28	$C_2H_4^+ + CO^+$	3.7	1.8	3
27	$C_2H_3^+$	8.4	8.0	2
26	$C_2H_2^+$	2.1	0.5	
15	CH_3^+	3.4	0.2	
14	CH_2^+	1.4	0	
		Total 97.6	97.6	

been discussed in detail in all papers dealing with the statistical theory [13, 14, 15, 16, 17, 21].

In our computations we have used an energy distribution that is constant between 10.5 eV and 17 eV and zero for higher energies. The breadth of this distribution amounts to only 6.5 eV and is thus narrower than the functions that have been used earlier. The computed mass spectrum is given in Table 2 together with the mass spectrum that has been observed by Friedman *et al.* [16] (see also [38, 39, 40, 41]).

The agreement between the observed and computed intensities in the table is surprisingly good for most of the fragments. The computed intensities for CH_3^+ and CH_2^+ are too low because these fragments are formed in larger quantities only above 19 eV and 23 eV, respectively. With another distribution function, extending to higher energy, better agreement would of course be obtained.

The small computed intensities for fragments 28 and 30 compared with the intensities obtained using electron impact are of great interest. From Fig. 2 it is evident that for each energy the intensities of these fragments are small compared with the corresponding intensity for fragment 43. The computed intensities of these fragments must therefore of necessity be small compared with the intensity of fragment 43, independently of the chosen energy distribution. It seems, therefore, that fragments 28 and 30 are formed to a much smaller extent using ion impact than using electron impact. This will be discussed in more detail below. It is characteristic for both these fragments that they are formed by loss of whole molecules, namely H_2O and CH_4, respectively.

Comparison with the statistical theory for mass spectra

Using the statistical theory for mass spectra, Friedman, Long, and Wolfsberg [16] have computed the mass spectrum for ethanol, which is reproduced in Fig. 3 with the alteration that IP for the molecular ion (10.5 eV) has been added to the inner excitation energy E, so that the horizontal axis denotes RE. In this graph the intensity for each fragment is zero for energies lower than AP and increases very

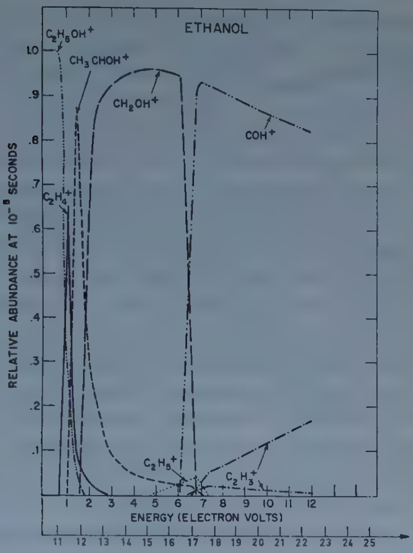


Fig. 3. Mass spectrum of C_2H_5OH as a function of energy computed by Friedman, Long, and Wolfsberg [16] using the statistical theory for mass spectra.

slowly with the energy for energies higher than AP. According to the theory, this is due to the assumption that the inner excitation energy is at first distributed over a very large number of vibrational degrees of freedom and after some time, because of statistical reasons, is concentrated in a certain chemical bond. Then dissociation of the molecule ion occurs at this bond. In Fig. 3 we obtain measurable intensities only for energies considerably higher than the mass-spectrometrically observed AP.

A comparison of our experimentally obtained curves in Fig. 2 with the theoretical curves shows, in some respects, poor agreement. For fragment 45 we have observed a high intensity for the energy 10.97 eV (N^+) and for the energy 11.26 eV (C^+) although these energies are immediately above the observed AP. Our experimental curve thus rises very steeply so that a maximum is already reached at about 0.2 or 0.4 eV above the AP. The theoretical curve in Fig. 3 on the other hand rises considerably slower and reaches its maximum at 0.9 eV above AP. This shows that if the statistical theory for mass spectra is to be applied to the dissociation giving fragment 45, the number of degrees of freedom N may not amount to the great number that is assumed in this theory, but must instead be a comparatively small number.

The same can be said regarding the fragments 29 and 27. For fragment 29 we have found considerable intensities at about 13.5 eV, although according to the theoretical curve measurable intensities should be obtained only above 15.5 eV. For fragment 27 we have observed considerable intensities at 14.5 eV although, according to the theoretical curve, measurable intensities should be obtained only above 17 eV.

Several authors have discussed the fact that the effective number of degrees of freedom in the dissociation of molecular ions usually seems to be a considerably smaller number than what is presumed in the statistical theory. Friedman, Long and Wolfsberg [42] have pointed out that the comparatively short tails observed in AP measurements suggest that the number of degrees of freedom is rather small. Chupka [2] has arrived at the same conclusions discussing measurements on *n*-propanol [1] and Kaminsky and Chupka [43] comparing their measurements and the curves theoretically computed for propane [13, 14]. Finally, when investigating some esters, King and Long [17] have questioned the validity of statistical theory for mass spectra for low excitation energies.

As the experiments seem to show that the inner excitation energy is distributed over a very small number of degrees of freedom in the molecule ion, its dissociation seems to be more or less directly determined by the weakening of a certain chemical bond in connection with the ionization of one of the electrons in the molecule. We shall therefore attempt to discuss the ionization of each of the different electrons in the molecule and for each ionization process consider the different dissociation processes that may follow from the primary ionization process.

These conclusions mean evidently that we assume that the statistical theory for mass spectra cannot be used for the interpretation of the formation of certain of the fragments from ethanol in the low energy range. A further support for this assumption are the double maxima that we have observed for curves 45 and 31. They show that, at least for the energies in question, the electron states are not so closely situated as the statistical theory presumes. This means that, at least in the cases that we have considered, the radiationless transitions that form the very foundation of the theory do not seem to take place to the extent that is assumed in this theory.

Dissociation of the molecule ion

As the statistical theory for mass spectra does not seem to be valid for the fragmentation of ethanol when the internal excitation energies are low, it seems necessary to try to interpret our measurements according to the principles that were used by different authors before the statistical theory was developed. Thus we assume that the dissociation of a certain bond in the molecule ion is caused by the ionization of a certain electron in the molecule. This electron is not necessarily localized in the bond that dissociates. As the dissociation processes may be interpreted as ordinary chemical reactions, most of the fragments formed will correspond to possible chemical compounds with C^+ and O^+ having the valency 3. The argument for this might be that such ions have especially low heats of formation according to Field and Franklin [21] (p. 87). In this manner the dissociation of some alcohols for very low supplied energies has already been discussed by Cummings and Bleakney [22], and the mechanism they proposed was elucidated particularly by Friedman and Turkevich [44].

An important consequence of this mechanism is that we are allowed to assume that chemically analogous compounds dissociate in an analogous manner after ionization of analogous electrons. It seems possible, in this way, to give an empirical systematics founded on chemical intuition in those cases where quantum chemical considerations cannot, at present, be used.

Structure of ethanol

The structure of ethanol may be deduced as follows. Mulliken [45] has given the structure of methanol

	$(2s)^2$	$[s]^2$	$[z']^2$	$[y']^2$	$[\pi]^{2+2}$	$(2x)^2$
Location	O	CH_3	OH	OC	CH_3	O
IP (Mulliken)	32	22	17.5	16	14.5	12.5

and for ethane [46]

	$[s a_1]^2$	$[s a_1]^2$	$[\pi e]^4$	$[\pi e]^4$	$[\sigma+\sigma, a_1]^2$
Location	CH_3	CH_3	CH_3	CH_3	CC
IP (Mulliken)	22	22	14.5	14.5	12
IP (This paper)	19	19	13.0	13.0	11.6

Combining these two structures, the following structure of ethanol is obtained:

	$(2s)^2$	$[s]^2$	$[s]^2$	$[\pi]^2$	$[z']^2$	$[y']^2$	$[\pi]^2$	$[\pi]^2$	$[\sigma+\sigma]^2$	$(2x)^2$
Location	O	CH_3	CH_2	CH_3	OH	CO	CH_3	CH_2	CC	O
IP (This paper)		19	19	15.6	15.3	13.1	13.0	13.0	11.6	10.5

The ionization potentials (IP) that have been used in this paper differ considerably from those used by Mulliken, as they are obtained from later measurements and computations.

IP 10.5 eV of $(2x)$ has been discussed above. This orbital is non-bonding and localized on the oxygen atom.

IP 11.6 eV of the bonding C–C orbital $[\sigma + \sigma]$ is simply the IP of ethane [21].

IP 13.0 eV of the $[\pi]$ orbitals in CH_3 in ethane have been obtained from measurements by Frost and McDowell [31]. They have shown that IP of these orbitals have approximately the same values for methane and all methyl halides. The accuracy of the estimated IP is therefore probably good. The value is supported by the theoretical computations by Hall [47], who has calculated the higher IP of ethane by means of the theory for equivalent orbitals. He has assumed that the constants a and b have the same values for methane and ethane and that certain other constants may be neglected. We have obtained the constants a and b from measurements by Frost and McDowell for methane [31] and have computed the following higher IP: two on each side of 13.2 eV and two near 17.8 eV.

One should expect the same values also for the $[\pi]$ orbitals in CH_3 and CH_2 in ethanol. Recently, however, Hall [48] has computed the IP's of the antisymmetric orbitals of ethanol: $(2x)$ 10.51 eV; CH_2 $[\pi]$ 13.01 eV; CH_3 $[\pi]$ 15.55 eV. According to Hall's computations the CH_3 $[\pi]$ orbital is delocalized and is influenced considerably by the oxygen. For the symmetric CH_3 $[\pi]$ orbital no computations have been performed, and therefore the value by Frost and McDowell, 13.0 eV, is used.

IP 13.1 eV of the bonding CO orbital $[y']$ is comparatively uncertain. We may assume that IP of this electron lies between IP of the corresponding electrons of the C—F and C—Cl bonds. Measurements by Frost and McDowell [31] have given 14.10 eV and 12.07 eV, respectively, of which we have used the mean.

IP 15.3 eV of the bonding OH orbital $[z']$ has been estimated here as the mean of the IP of the two bonding OH orbitals in H_2O, which have been measured to be 14.35 eV and 16.34 eV, respectively, by Sugden and Price [49], and by Frost and McDowell [50].

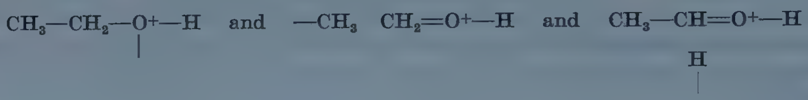
IP 15.6 eV of the $[\pi]$ orbitals in CH_3 is taken from Hall's computations (see above).

IP 19 eV of the bonding CH_3 and CH_2 orbitals $[s]$ was obtained from Frost and McDowell's measurements [31]. They have shown that IP of these orbitals have approximately the same values for methane and three methyl halides.

For the $(2s)$ orbital in the oxygen atom IP is high. For the corresponding orbital in H_2O it has been estimated by Mulliken [45] as 32 eV and by Ellison and Shull [51] as 36 eV.

Discussion of the dissociation processes

When the supplied energy amounts to 10.5 eV or somewhat more, the non-bonding oxygen electron ($2x$) is ionized [22, 52, 44, 2]. The molecule ion with mass 46 is stable according to our curves although it does not correspond to any conventional chemical compound but must be denoted as a charged free radical. As the ionized oxygen atom must be presumed to have the valency three we have reason to assume that there is a tendency for the third bond to interact with the other parts of the molecule. Such an interaction implies a tendency towards formation of a double bond between C and O^+, which means that at the same time the other bonds of the carbon atom are weakened. We can consider that we have obtained three resonant structures:



$$CH_3—CH_2—O^+—H \quad \text{and} \quad —CH_3 \;\; CH_2{=}O^+—H \quad \text{and} \quad CH_3—CH{=}O^+—H \;\; H$$

which means a weakening of the C—C and C—H bonds, respectively [53]. We therefore expect that either a hydrogen atom or a methyl radical leaves the molecular ion, which, however, cannot happen until the energy is a little higher than 10.5 eV. (A third possibility is, of course, addition of a hydrogen atom so that an ion with mass 47 is formed.)

When the supplied energy exceeds 10.8 eV, dissociation of a hydrogen atom occurs and we obtain fragment 45 with structure $CH_3—CH{=}O^+—H$ (cf. Fig. 4). Mass spectrometric analysis of deuterated ethanol [39, 16] has proved that the lost hydrogen atom originates from the CH_2 group. As soon as this dissociation is no longer energetically forbidden, it takes place more or less completely so that in our graph curve 46 is rapidly decreasing while curve 45 is rapidly increasing. After the passage of the maximum at about 11.25 eV, curve 45 decreases rapidly again. The main explanation is probably that the molecule ion dissociates with loss of a methyl radical instead. Further, it is possible that as ($2x$) is a non-bonding electron, only a small energy can be absorbed by the molecule as vibrational energy when ionizing this electron.

When the supplied energy exceeds 11.25 eV, the dissociation may occur in another manner. A methyl radical is lost and fragment 31 with structure $CH_2{=}O^+—H$ [39, 16] is obtained. This is evident from curve 31, which, above this energy, is rising steeply to a maximum at about 12.1 eV. As supporting evidence for this process, in which the ionization of a lone pair electron on the oxygen atom is followed by loss of a methyl group, the following may be mentioned. For propylamine, $CH_3—CH_2—CH_2—NH_2$, Chupka [2] using photon impact [1] has determined AP for the molecule ion and $CH_2NH_2^+$ to be 8.8 eV and 9.2 eV, respectively. He presumes that "the ionization near threshold probably corresponds to removal of one of the non-bonding p electrons of the nitrogen atom" and considers the vibrations excited in the ionization. He finds, however, that "it is difficult to see how these vibrations could lead very directly to the observed dissociation of the C—C bond which does not even involve the nitrogen atom". Further the dissociation at 9.2 eV cannot be explained by the ionization of a bonding C—C electron as the IP of such an electron is considerably higher (about 11.2 eV). If, however, we assume that the ionization of a lone pair electron in the NH_2 group weakens the strength of the bond between the two neighbouring carbon atoms, this dissociation of propylamine seems immediately understandable. This may also be considered as an indirect proof of the importance

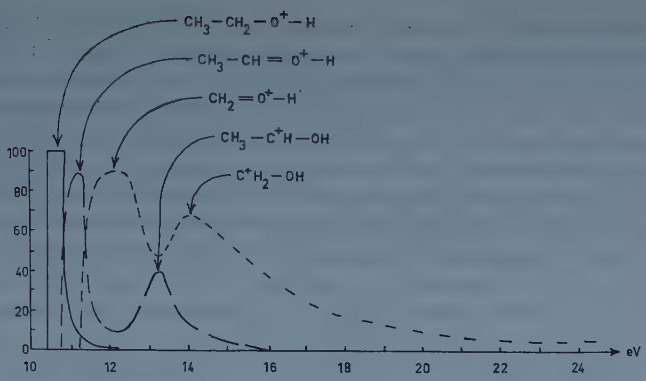


Fig. 4. Possible interpretation of the main peaks in the mass spectrum of C_2H_5OH.

of the corresponding process in the alcohols. The same discussion may be used for ethylamine $CH_3CH_2NH_2$, for which Collin [54] has determined AP for the molecule ion and CH_2NH_2 to be 9.6 eV and 10.2 eV, respectively.

Having discussed the processes following ionization of the $(2x)$ electron, we shall now discuss the ionization of the C—C electron $[\sigma + \sigma]$. As mentioned above its IP is taken to be 11.6 eV, which is simply the IP of ethane. As the ethane here is substituted, the corresponding IP of ethanol is probably somewhat lower. Of course it is possible for this electron to be ionized when the appropriate energy is supplied; the probability for the process in question, however, cannot be estimated and cannot be deduced from our curves. It is evident only that the molecular ion which has been formed at this energy is not stable but dissociates giving either fragment 45 or fragment 31. Of course we expect that the ionization of a C—C electron ought to cause a weakening of the C—C bond so that the following dissociation should mean a split of this bond. However, a comparison with the decomposition of C_2H_6 shows that this cannot be the case. In C_2H_6 the corresponding electron is ionized at 11.6 eV, but CH_3^+ is not obtained until 13.9 eV, and instead $C_2H_5^+$ is obtained after loss of an H atom with AP 12.8 eV. Since IP for an electron in the CH_3 group seems to be about 13.0 eV, it seems to be impossible to make a distinct difference between the dissociation of ethane caused by the ionization of a C—C electron and the dissociation caused by the ionization of a C—H electron. It seems to be evident that the localization of these electrons in C_2H_6 is incomplete. We must therefore discuss the C—C electrons and the C—H electrons simultaneously. With this introduction we are now able to discuss the analogous decomposition of C_2H_5OH. After the ionization of a C—C electron or a C—H electron, an H atom is lost and fragment 45 is obtained with an AP which, according to the analogy with C_2H_6, we can assume to be about 12.8 eV. The structure of the fragment might be expected to be $C^+H_2—CH_2—OH$ or $CH_3—C^+H—OH$. The first structure disagrees with the experimental results with deuterated ethanol and must therefore be omitted. The cause for this is possibly that IP of the $[\pi]$ orbital in CH_3 is high compared with IP of the CH_2 and CC orbitals. At higher energy the C—C bond dissociates with an AP that, from the analogy with the decomposition of C_2H_6, may be estimated at 13.9 eV. At this energy we thus expect fragment 31 with structure $C^+H_2—O—H$. These predictions agree well with our curves, which for mass 45 have a peak beginning at 12.8 eV, and for mass 31 have a peak beginning at 13.5 eV. As a further experimental support the following may be mentioned. Friedman *et al.* [16] have assumed that the fragment $C_2H_3^+$ is formed from fragment 45 by loss of H_2O. This assumption is supported by our curves, according to which the sum of the intensities of fragments 45 and 27 is changing rather slowly near AP for $C_2H_3^+$. It is reasonable to conclude that fragment 45 most probably has the structure $CH_3—C^+H—OH$ in this energy range, as it is easy to imagine that $CH_2=C^+H$ may be formed from the former ion by loss of H_2O. Had the structure been $CH_3—CH=O^+—H$, it would have been difficult to explain this decomposition. The mechanism for formation of $C_2H_3^+$ is supported by the mass spectrum of CH_3CD_2OH, obtained by Momigny [39], in which the corresponding fragment seems to have the formula $C_2H_2D^+$. The same mass spectrum has also been measured by Friedman *et al.* [16], but their results are more difficult to interpret. Further, the proposed decomposition is supported by measurements on *i*-propanol [44, 55, 56]. This compound seems to dissociate in the same manner as ethanol, giving fragment 45 in large quantities by loss of CH_3, as well as fragment 27. From $(CH_3)_2CDOD$ and $(CH_3)_2CDOH$ mainly C_2H_2D is obtained, while $(CH_3)_2CHOD$ gives C_2H_3 and $(CD_3)_2CHOH$ gives mainly C_2D_2H. Finally, we must discuss what happens after the ionization of a C—C electron if the supplied energy is between 11.6 and 12.8 eV. For propane the molecular ion is stable in this energy range, but for ethanol it follows from our curves that the molecular ion is unstable and decomposes, forming fragment 45 or fragment 31. This decomposition cannot be explained by any of the mentioned processes. We must therefore assume a rearrangement of the electrons in the molecular ion, so that afterwards the structure becomes $CH_3—CH_2—O^+—H$ in this energy range. It is possible that the excess energy, which amounts to the difference between the IP of the C—C electron and the O electron, is transformed into vibrational energy in the C—C bond. This dissociation of the molecule ion will therefore take place mainly by C—C split in the manner discussed above, giving fragments $CH_2=O^+—H$ in good correspondence with the maximum of our curve 31 at 12.1 eV. This rearrangement of the electron energy can be said to be analogous to the rearrangements of the vibrational energy considered in the statistical theory for mass spectra.

We shall now discuss the ionization of the bonding C—O electron [y'] at about 13.1 eV. From our measurements it follows that at this energy the molecule ion is unstable. The dissociation can be assumed to give either $C_2H_5^+$ or OH^+. It is of course necessary for the processes to be energetically possible. Friedman *et al.* [16] have computed AP of the first process to be 12.65 eV using thermochemical methods. For the second process AP must be approximately 17.9 eV as IP of OH is about 5 eV higher than IP of C_2H_5 (see [21], p. 106, and [18]). Only the first process is thus energetically possible at low energies. We therefore expect to obtain $C_2H_5^+$ ions at about 12.65 eV and higher energies. This agrees with our graphs and with the earlier AP measurements. The fragments 29 are assumed to have the structure $C_2H_5^+$ and not COH^+ in this energy range in agreement with the energetical computations by Friedman *et al.* (according to Cox [25] $C_2H_5^+$ and COH^+ have approximately equal AP). Several investigations of metastable ions have shown that $C_2H_5^+$ may decompose to $C_2H_3^+$. This process is therefore probably of importance also in the decomposition of the ethanol molecule ion. The probability of the process may be deduced from our curves since the sum of the intensities of fragments $C_2H_5^+$ and $C_2H_3^+$ ought to be fairly constant for energies near AP of $C_2H_3^+$, (cf. Fig. 3). From our curves is evident, however, that the intensity of $C_2H_3^+$ is much larger than that of $C_2H_5^+$, independently of the interpretation of the fragments with mass 29. The decomposition of $C_2H_5^+$ to $C_2H_3^+$ is therefore probably of small importance in the fragmentation of the ethanol molecular ion (cf. [57]). $C_2H_3^+$ is apparently formed mainly by some other process as discussed above.

After this discussion of the ionization of some electrons we will now discuss some other fragments.

Fragment 43 is probably formed from fragment 45 by loss of H_2. As we have shown that fragment 45, in this energy range, probably has the structure $CH_3{-}C^+H{-}OH$, fragment 43 ought to have one of the following structures:

$$CH_3{-}C^+{=}O \quad \text{or} \quad \lfloor CH_2{-}C^+H{-}O \rfloor \quad \text{or} \quad CH_2{=}C^+{-}OH$$

Friedman and Turkevich [44] have shown that when fragment 43 is obtained from *i*-propanol, the last structure is of secondary importance. It may probably be neglected as well when discussing ethanol. According to Momigny's measurements on CH_3CD_2OH [39] the first structure is probably of somewhat less importance than the second. No explanation can be given of the fact that the second structure probably predominates. According to the following computations all three processes seem to be approximately equivalent energetically. From our curves AP for $CH_3{-}C^+H{-}OH$ can be estimated at about 12.8 eV. Using $D(CH) = 4.26$ eV, $D(OH) = 4.75$ eV, $D(C{-}O) = 3.43$ eV, $D(C{=}O) = 7.50$ eV, $D(C{-}C) = 3.49$ eV, $D(C{=}C) = 6.30$ eV, and $D(H_2) = 4.48$ eV we obtain

$$AP\,(CH_3{-}C^+{=}O) = 12.8 + 4.26 + 4.75 + 3.43 - 7.50 - 4.48 = 13.26\ \text{eV}$$

$$AP\,(\lfloor CH_2{-}C^+H{-}O \rfloor) = 12.8 + 4.26 + 4.75 - 3.43 - 4.48 = 13.90\ \text{eV}$$

$$AP\,(CH_2{=}C^+{-}OH) = 12.8 + 4.26 + 4.26 + 3.49 - 6.30 - 4.48 = 14.03\ \text{eV}$$

All three processes are apparently energetically possible as our curve 43 begins to rise at about 15 eV.

CH_3^+ is assumed by Friedman *et al.* [16] to be formed by dissociation of CH_3CHOH^+. Our measurements show that this hypothesis is probably not correct, for the sum of the intensities of fragments 45 and 15 should then be approximately independent of the energy in the range near AP of CH_3^+. According to our curves, however, this sum has a minimum there approximately equal to zero. We must therefore try to find some other fragment that might be the source of CH_3^+. From Fig. 2 we find that the only possibility is fragment 43, which gives CH_3^+ and CO. AP for this process can be computed thermochemically:

$$\begin{aligned} A\,(CH_3{}^+) &= \Delta H_f(CH_3{}^+) + \Delta H_f(CO) + \Delta H_f(H_2) + \Delta H_f(H) - \Delta H_f(C_2H_5OH) \\ &= \quad 262 \quad - \quad 26 \quad + \quad 0 \quad + \quad 52 \quad + \quad 56 \\ &= 344\ \text{kcal/mol} = 15.0\ \text{eV}. \end{aligned}$$

As the experimental values are higher, the proposed dissociation process does not seem to be unreasonable. As further support, we may mention that CH_3CO^+ and CH_3^+ are simultaneously remarkably intense in the mass spectra of several molecules as for instance acetone [56] and methyl acetate [17]. (In the latter case King and Long assume a more direct dissociation process.) Nor does the proposed mechanism for formation of CH_3^+ seem to be inconsistent with the results of the investigations of the fragmentation of acetaldehyde [58, 59]. Of course there is always the possibility that CH_3^+ is formed directly from the molecular ion by a simple C—C bond split. In that case we should expect the AP at about 13.7 eV, as D(C—C) = 3.7 eV and I(CH_3) = 10.0 eV. The difference between this theoretical and the experimental AP may be explained by the assumption that the dissociation takes place with kinetic energy (cf. [25]), but it is possibly more correct to assume that CH_3^+ is not at all formed in this manner, and that the dissociation of the C—C bond gives only fragment 31, as this has a lower IP. The formation of CH_3^+ seems therefore to proceed according to Stevenson's rule [60] (see [61] and [21], p. 84), according to which with a molecule R_1R_2 where $IP_{R_1} < IP_{R_2}$ the process $R_1R_2^+ \rightarrow R_1^+ + R_2$ will occur in such a way that R_1^+ and R_2 are in their ground states; on the other hand the process yielding R_2^+ will usually occur with excitation, often by formation of several neutral fragments. The formation of CH_3^+ from CH_3CO^+ can be understood if resonance is assumed between the following structures which mean a weakened C—C bond: $CH_3—C^+{=}O$ and $CH_3^+\ C{=}O$ and possibly also $CH_3—C{\equiv}O^+$. On the other hand formation of CH_3^+ from $\underline{\lvert CH_2—C^+H—O \rvert}$ must mean rearrangement. From CH_3CD_2OH fragments with mass 15 ought to be obtained in the first case, but in the second case the corresponding fragments should have mass 16. The mass spectrum obtained by Momigny [39] suggests that both processes are of importance as both fragments seem to appear. Finally it must be pointed out that the processes for formation of CH_3^+, which we have discussed here, are thought to be valid only for energies near AP of CH_3^+.

It was mentioned above that fragments 28 and 30 seem to be formed to a smaller extent using ion impact than using electron impact. In regard to fragment 28, Friedman *et al.* [16] have computed that $C_2H_4^+$ ought to be obtained as a high and narrow peak at about 11.5 eV with AP at about 11 eV. However, we have not been able to find any appreciable quantities of this fragment using any of the incident ions. The atomic ions that we have used, for instance C^+, P^+, and S^+, have several RE in this energy range, and therefore the peak ought to have been observed if it had existed. This fragment seems therefore to be formed in electron impact mainly in such a manner that it cannot be obtained by charge exchange in ion impact with a comparable intensity. A possible explanation is that $C_2H_4^+$ is formed according to process 4 discussed in the introduction. This means that the molecular ion which gives this fragment can be formed only via a highly excited state of the molecule and not by direct ionization of the molecule. This interpretation is supported by observations of the corresponding fragment with mass 42 from *n*-propanol by Hurzeler *et al.* [1], and Chupka [2] in their investigations using photon impact. The intensity of the fragment was large and its AP only about 0.4 eV higher than the AP of the molecular ion.

The same seems to be valid for fragment 30 although no measurements using photon impact have been made.

The last fragment we shall mention is COH^+. Friedman *et al.* have suggested that COH^+ is formed from CH_2OH^+. This assumption is supported by the mass spectrum of CH_3CD_2OH obtained by Momigny [39] in which peak 30 (7.4 units) must be interpreted as CDO^+ and peak 31 (3.0 units) as CH_3CD_2. (The sum of the intensities agrees with the intensity of peak 29 in the mass spectrum of C_2H_5OH and the ratio between the intensities with the ratio in Table 2 in [16].) The assumption is not in disagreement with our measurements.

As at higher energies the number of experimental points is very small, it is impossible to draw definite conclusions in this energy range. It is therefore impossible to discuss the ionization of the inner electrons [*z*′], [*s*], and (2*s*), and it is also impossible to discuss the application of the statistical theory for mass spectra, in this higher energy range, on the basis of our measurements.

Further comments on the statistical theory

The mechanism that we have used above for the study of the fragmentation of the ethanol molecule ion has previously been criticised by several authors [62, 14,13] (see also [21], p. 69). They have pointed out that if one assumes that the decomposition of the molecule ion occurs at the bond from which an electron is removed, then the intensity of an ion formed by breaking a particular type of bond should depend greatly upon the relative number of bonds of this type in a molecule. For example, the number of $C_nH_{2n+1}^+$ ions formed from paraffin hydrocarbons should show the same relation to the total number of ions formed as the number of C—H bonds shows to the total number of bonds. This is not true, as may be seen from the data for the dissociation of propane, *n*-butane, and *n*-heptane.

The dissociation processes discussed in this paper for ethanol show, however, that there is a possibility that a certain chemical bond can be broken as a consequence of the ionization of an electron that is *not* localized in this bond. This third possibility does not seem to have been considered by the authors mentioned above. The necessity for a statistical theory is therefore not justifiable on the basis of such an argument.

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REFERENCES

1. Hurzeler, H., Inghram, M. G., and Morrison, J. D., J. Chem. Phys. *28*, 76 (1958).
2. Chupka, W. A., J. Chem. Phys. *30*, 191 (1959).
3. Weissler, G. L., Samson, J. A. R., Ogawa, M., and Cook, G. R., J. Opt. Soc. Am. *49*, 338 (1959).
4. Morrison, J. D., J. Appl. Phys. *28*, 1409 (1957); Revs. Pure and Appl. Chem. *5*, 22 (1955).
5. Dorman, F. H., Morrison, J. D., and Nicholson, A. J. C., J. Chem. Phys. *32*, 378 (1960).
6. Lagergren, C. R., Ph.D. Thesis, Univ. of Minnesota, 1955. Univ. Microfilm, Ann Arbor, Michigan, Doctoral Dissertation Series Publ. No. 15940.
7. Gustafsson, E., and Lindholm, E., Arkiv f. Fysik, *18*, 219 (1960).
8. Lindholm, E., Proc. Phys. Soc. (Lond.) *A 66*, 1068 (1953).
9. Lindholm, E., Institute of Petroleum, Conference on Applied Mass Spectrometry, London 1953.
10. Lindholm, E., Z. Naturforsch. *9a*, 535 (1954).
11. Lindholm, E., Arkiv f. Fysik *8*, 257 (1954).
12. Lindholm, E., Arkiv f. Fysik *8*, 433 (1954).
13. Rosenstock, H. M., Wallenstein, M. B., Wahrhaftig, A. L., and Eyring, H., Proc. Natl. Acad. Sci. U.S. *38*, 667 (1952).
14. Rosenstock, H. M., Wahrhaftig, A. L., and Eyring, H., "The Mass Spectra of Large Molecules, II—The Application of Absolute Rate Theory", Tech. Rept. No. II, June 25, 1952. Univ. of Utah, Inst. for Study of Rate Processes, Salt Lake City.
15. Kropf, A., Eyring, E. M., Wahrhaftig, A. L., and Eyring, H., J. Chem. Phys. *32*, 149 (1960).
16. Friedman, L., Long, F. A., and Wolfsberg, M., J. Chem. Phys. *27*, 613 (1957).
17. King, A. B., and Long, F. A., J. Chem. Phys. *29*, 374 (1958).
18. Collin, J., Bull. Soc. Roy. Sci. Liège *25*, 520 (1956).

19. Ewald, H., and Hintenberger, H., Methoden und Anwendungen der Massenspektroskopie, Verlag Chemie, Weinheim/Bergstrasse, 1953.
20. Lindholm, E., Rev. Sci. Instr. *31*, 210 (1960).
21. Field, F. H., and Franklin, J. L., Electron Impact Phenomena, Academic Press, New York, 1957.
22. Cummings, C. S., and Bleakney, W., Phys. Rev. *58*, 787 (1940).
23. Kambara, T., and Kanomata, I., Proc. Phys. Soc. Japan *4*, 71 (1949); see ref. [21].
24. Morrison, J. D., and Nicholson, A. J. C., J. Chem. Phys. *20*, 1021 (1952).
25. Cox, B. C., Diss. Liverpool; see Craggs, J. D., and Massey, H. S. W., Encyc. of Phys., Vol. XXXVII/1, 314 (1959), p. 384. For some fragments Cox has observed several AP.
26. Hagstrum, H. D., Phys. Rev. *104*, 309 (1956).
27. Martin, W. C., J. Opt. Soc. Am. *49*, 1071 (1959).
28. Watanabe, K., J. Chem. Phys. *22*, 1564 (1954).
29. Moore, C. E., Atomic Energy Levels, Natl. Bur. Standards Circ. 467, Vol. III, 1958.
30. Hasted, J. B., J. Appl. Phys. *30*, 25 (1959).
31. Frost, D. C., and McDowell, C. A., Proc. Roy. Soc. (Lond.) *A 241*, 194 (1957).
32. Bates, D. R., and Massey, H. S. W., Phil. Mag. *45*, 111 (1954).
33. Hasted, J. B., and Smith, R. A., Proc. Roy. Soc. (Lond.) *A 235*, 354 (1956).
34. Boyd, T. J. M., and Moiseiwitsch, B. L., Proc. Phys. Soc. (Lond.) *A 70*, 809 (1957).
35. Flaks, I. P., and Solov'ev, E. S., Soviet Phys.-Tech. Phys. *3*, 564 (1958).
36. Melton, C. E., and Rudolph, P. S., J. Chem. Phys. *30*, 847 (1959).
37. Flaks, I. P., and Solov'ev, E. S., Soviet Phys.-Tech. Phys. *3*, 577 (1958).
38. Catalog of Mass Spectral Data, Am. Petroleum Inst. Research Project 44, Carnegie Institute of Technology, Pittsburgh.
39. Momigny, J., Bull. Soc. Roy. Sci. Liège *24*, 111 (1955).
40. Collin, J., Bull. Soc. Roy. Sci. Liège *25*, 441 (1956).
41. Gifford, A. P., Rock, S. M., and Comaford, D. J., Anal. Chem. *21*, 1026 (1949).
42. Friedman, L., Long, F. A., and Wolfsberg, M., J. Chem. Phys. *26*, 714 (1957).
43. Kaminsky, M. S., and Chupka, W. A., Bull. Am. Phys. Soc. *4*, 235 (1959).
44. Friedman, L., and Turkevich, J., J. Am. Chem. Soc. *74*, 1666 (1952).
45. Mulliken, R. S., J. Chem. Phys. *3*, 506 (1935).
46. Mulliken, R. S., J. Chem. Phys. *3*, 517 (1935).
47. Hall, G. G., Proc. Roy. Soc. (Lond.) *A 205*, 541 (1951).
48. Hall, G. G., private communication.
49. Sugden, T. M., and Price, W. C., Trans. Faraday Soc. *44*, 108 (1948).
50. Frost, D. C., and McDowell, C. A., Can. J. Chem. *36*, 39 (1958).
51. Ellison, F. O., and Shull, H., J. Chem. Phys. *21*, 1420 (1953).
52. Walsh, A. D., Trans. Faraday Soc. *42*, 56 (1946); *43*, 60 (1947).
53. Lester, R. G., Joint Conference on Mass Spectrometry, Pergamon Press, London, 1959.
54. Collin, J., Bull. Soc. Chim. Belges *62*, 411 (1953).
55. Condon, F. E., McMurry, H. L., and Thornton, V., J. Chem. Phys. *19*, 1010 (1951).
56. Condon, F. E., J. Am. Chem. Soc. *73*, 4675 (1951).
57. Lampe, F. W., and Field, F. H., J. Am. Chem. Soc. *81*, 3238 (1959).
58. Brinton, R. K., and Blacet, F. E., J. Chem. Phys. *17*, 797 (1949).
59. McDowell, C. A., and Warren, J. W., Mass Spectrometry, p. 27, Institute of Petroleum, London, 1952.
60. Stevenson, D. P., Discussions Faraday Soc. *10*, 35 (1951).
61. Krauss, M., Wahrhaftig, A. L., and Eyring, H., Ann. Rev. Nuclear Sci. *5*, 241 (1955), p. 259.
62. Wallenstein, M. B., Wahrhaftig, A. L., and Eyring, H., "The Mass Spectra of Large Molecules, I.—Saturated Hydrocarbons", Tech. Rept. No. I, June 15, 1951, Univ. of Utah, Inst. for Study of Rate Processes, Salt Lake City.
63. Martin, W. C., and Corliss, C. H., J. Opt. Soc. Am. *48*, 865 (1958).

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